


average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering the collection of information. Send comments regarding this burden estimate or any other aspect of this form to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Avenue, Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 2, 1994		3. REPORT TYPE AND DATES COVERED January 1, 1993-March 2, 1994	
4. TITLE AND SUBTITLE Deuterium NMR Study of the Dynamics of Solid State Polymethylphenylsilane				5. FUNDING NUMBERS PE-N0014-91 PR-1274	
6. AUTHOR(S) R.D. O'Connor, Frank D. Blum, E. Ginsburg* and R.D. Miller*					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Missouri-Rolla Department of Chemistry Rolla, MO 65401 ATTN: Frank D. Blum				8. PERFORMING ORGANIZATION REPORT NUMBER UMR-FDB- 36	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research - Code 5000 Chemistry Division 800 Quincy Street Arlington, VA 22217 ATTN: Kenneth J. Wynne				94-08662 	
11. SUPPLEMENTARY NOTES For publication in Polymer Preprints					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited - Approved for unlimited public release				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Polymethylphenylsilane-d <sub>3</sub> (PMPS-d <sub>3</sub> ) has been synthesized and labelled in the methyl position. Its dynamics were then probed with <sup>2</sup> H NMR. Quadrupole echo spectra were acquired from 24 to 100 °C with varying echo delays. At low temperature, the spectra are consistent with methyl rotation only. As the temperature increased, the spectra appeared to be a superposition of a rigid and mobile component with the mobile component gradually developing over a 50° temperature range. There is only a small variation of line shape with echo delay suggesting that there are few motions in the intermediate motion range. Thus, PMPS-d <sub>3</sub> may have a bimodal distribution of correlation times. In addition, the NMR probe of the T <sub>g</sub> is consistent with the material glassing over a broad range of temperatures.					
14. SUBJECT TERMS				15. NUMBER OF PAGES 3	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
				20. LIMITATION OF ABSTRACT	

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1274

R&T Code 413m005---04

Technical Report # UMR-FDB-36

Deuterium NMR Study of the  
Dynamics of Solid State Polymethylphenylsilane

by

R.D. O'Connor, Frank D. Blum, E. Ginsburg\* and R.D. Miller\*

Department of Chemistry and Materials Research Center  
University of Missouri-Rolla  
Rolla, MO 65401

(314) 341-4451

\* IBM Almaden Research Laboratory  
650 Harry Rd.  
San Jose, CA 95120

Prepared for Publication in

*Polymer Preprints*

March 2, 1994

Accession For	
NTIS	<input checked="" type="checkbox"/>
CRA&I	<input checked="" type="checkbox"/>
DTIC	<input type="checkbox"/>
TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By .....	
Distribution /	
Availability Codes	
Dist	Avail and / or Special
A-1	

Reproduction in whole, or in part, is permitted for any purpose of the  
United States Government.

This document has been approved for public release and sale: its  
distribution is unlimited.

# Deuterium NMR Study of the Dynamics of Solid State Polymethylphenylsilane

Robert D. O'Connor\*, Frank D. Blum\*, Eric Ginsburg†, and Robert D. Miller†

\*Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65401

†IBM Almaden Research Laboratory, 850 Harry Rd, San Jose, CA 95120

†Paper and Reversal Chemistry Lab, B82, Mail Code 02103, Eastman Kodak, Rochester, NY 14650-2103

## Introduction

Polysilanes are relatively new materials. Their properties differ from similar carbon based polymers because of the Si-Si bond. The bond is more sensitive to UV radiation and longer than a C-C bond. The bond's UV sensitivity makes polysilanes candidates for microlithography and related applications.<sup>1,2</sup> Its increased length allows for more diverse side chain substitution. These enhanced properties might be exploited though an understanding of the polymers' structure and dynamics. The structure of several polysilanes have recently been investigated.<sup>1,2</sup> In this work, we report investigations of the dynamics of solid state polymethylphenylsilane-d<sub>3</sub> (PMPS-d<sub>3</sub>) with <sup>2</sup>H NMR.

We have deuterated the methyl group on PMPS in an effort to study its backbone motion. Using the quadrupole echo pulse sequence, we have acquired <sup>2</sup>H spectra from 24 to 100 °C with varying echo delay. The expected spectra should be indicative of normal methyl rotation with backbone motion superimposed. If the backbone motion is slow, there should be no change in the spectra. If it is fast, the spectra should be further narrowed, perhaps converging to a liquid-like line. If the backbone motion is on the order of the echo delay, the line shape will be a function of the delay. Finally, a distribution of motion will result in a superposition of the above cases.

## <sup>2</sup>H NMR

In addition to the Zeeman interaction, <sup>2</sup>H NMR of solids is dominated by the coupling of the nuclear electric quadrupole with the electric field gradient (EFG) at the <sup>2</sup>H nucleus. For <sup>2</sup>H bonded to carbon, to a good approximation the EFG is axial symmetric along the bond and the frequencies of <sup>2</sup>H's two NMR transitions are:<sup>3,4</sup>

$$\omega_{\pm} = \omega_0 \pm \frac{3}{4} Q_{cc} (3\cos^2\theta - 1) \quad (1)$$

where  $\omega_0$  is the Larmor frequency,  $Q_{cc}$  is the quadrupole coupling constant, and  $\theta$  is the polar angles describing the orientation of the magnetic field with respect to the principal axis of the EFG tensor. For a non-crystalline solid, the frequencies must be weighted by the fraction of bonds with angle  $\theta$ . This convolution results in the powder patterns shown in Figure 1.

For a completely rigid aliphatic deuteron the splitting between the singularities (or horns) is about 125 kHz with the entire spectrum covering 250 kHz. The quadrupole echo sequence (QES) overcomes the receiver dead time problem associated with broad lines.<sup>5</sup> The QES is two 90° pulses 90° out of phase with each other and separated by a delay,  $d$ . With this sequence, a signal echo appears at  $2d$  from the initial pulse. To avoid intensity loss from relaxation,  $d$  is usually from  $10^{-5}$  to  $10^{-6}$  s. The QES reproduces the original FID as long as the motion is much faster or much slower than  $d$ . Motion with correlation times on the order of  $d$  result in an intensity loss which depends on  $d$ , frequency, and type of motion.<sup>6</sup>

Though the QES reproduces the original signal for rapid motion, rapid motion (correlation times  $\ll \delta^{-1}$ ) will result in an average EFG tensor and consequently an average coupling constant. For a freely rotating, but otherwise rigid methyl group, the spectrum retains its shape but the splitting is reduced to  $(3\cos^2\beta - 1)/2$  where  $\beta$  is the angle of the rotation axis to the <sup>2</sup>H bond. This reduces the splitting from 125 kHz to

about 42 kHz. Other motions, besides simple rotations, may alter the line shape as well.

## Experimental

**Synthesis:** PMPS-d<sub>3</sub> was prepared by first synthesizing PhSiH<sub>2</sub>Cl, converting it to PhSiH<sub>2</sub>CD<sub>3</sub> through a Grignard reaction, then chlorination to PhSiCl<sub>2</sub>CD<sub>3</sub>, and finally polymerization with Na to PMPS-d<sub>3</sub>.

**Phenyltrideuteriomethylsilane:** In an oven dried, argon filled 3-neck flask, 9 mmol of PhSiH<sub>2</sub>Cl, prepared as described by H. Schidbaur<sup>7</sup>, was dissolved in 100 ml of dry THF. After cooling to 0 °C, 100 ml of a 1 M solution of CD<sub>3</sub>MgI in diethylether (Et<sub>2</sub>O) was added over a period of 30 minutes. The white mixture was stirred for an additional 30 minutes and then washed with water. The aqueous phase was extracted with Et<sub>2</sub>O and the combined organic phase was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated. The remaining THF was distilled off under argon at ambient pressure, then PhSiH<sub>2</sub>CD<sub>3</sub> was distilled at 135-140 °C into a Kontes storage flask equipped with a teflon valve.

**Dichlorophenyltrideuteriomethylsilane:** In an argon filled flask, 8.7 g of PhSiH<sub>2</sub>CD<sub>3</sub>, 75 ml of CCl<sub>4</sub>, and a few milligrams of Pt(II)Cl<sub>2</sub> were refluxed at 80 °C for 27 hours. The mixture was concentrated to a brown oil, CaH<sub>2</sub> was added, and PhSiCl<sub>2</sub>CD<sub>3</sub> was distilled at 60-70 °C/10 mm Hg to yield 7.0 g. GC indicated a purity of 96.8% with several close

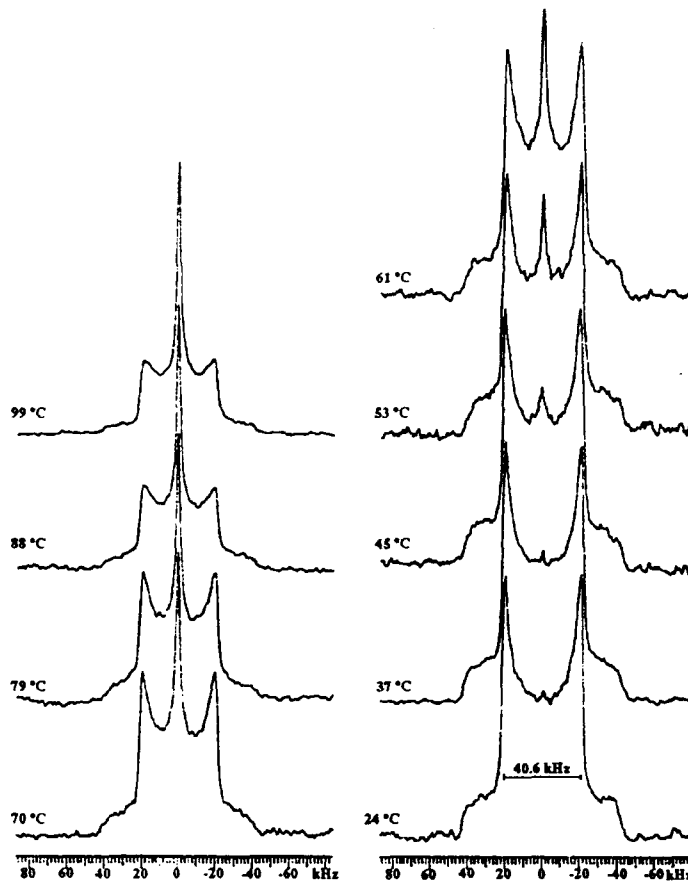


Figure 1. Solid echo spectra at different temperatures for PMPS-d<sub>3</sub>

boiling impurities.

**Polymerization:** 79 mmol of Na spheres were dispersed in 40 ml of dry toluene. The mixture was heated to 65 °C and, while stirring, 36 mmol of PhSiCl<sub>2</sub>CD<sub>3</sub> dissolved in 10 ml of dry toluene was added dropwise. The mixture became purple about half way through the addition. The mixture was stirred for an additional hour at 65 °C. The heat bath was removed and 20 ml of dried toluene, 5 ml iso-propyl alcohol, and then 60 ml of toluene were added in succession. The mixture was

stirred for 5 minutes and filtered with an additional 40 ml of toluene added to wash the salt residue. The organics were washed with water and dried with  $\text{MgSO}_4$ . After adding 100 ml of methanol, a cloudy suspension resulted and 12 hours later the precipitate was collected and vacuum dried to yield 40 mg of PMPS- $\text{d}_3$ ,  $M_n = 426 \text{ kg/mol}$  and  $\text{PD} = 2.3$  as compared to polystyrene (GPC).

**NMR measurements:** The  $^2\text{H}$  NMR experiments were performed at 30.7 MHz with a Varian VXR spectrometer. The temperature was maintained to  $\pm 2^\circ\text{C}$  by an Oxford VTC4 VT unit. Using the QES, the spectra were acquired with 4k points, 8k scans, a digitization rate of 2 MHz, a  $2.4 \mu\text{s}$   $90^\circ$  pulse width, an echo delay of  $35 \mu\text{s}$ , and a scan repetition rate of 0.5 s. With this repetition rate, the spectra are fully relaxed. The sample was allowed to equilibrate for at least 30 minutes at each temperature. The FID's were shifted to the echo maximum, zero filled to 8k, and Fourier transformed with 1000 Hz line broadening.

## Results

Figure 1 shows the spectra of PMPS- $\text{d}_3$  from 24 to  $100^\circ\text{C}$ . At low temperatures, the spectrum is a reduced powder pattern with a splitting of 40.6 kHz - the expected pattern for a rotating methyl group with no other motion. As the temperature increases, a mobile component, the narrower central peak, gradually emerges from the rigid component. As it builds, the rigid component retains its 40 kHz splitting. This gradual appearance of a mobile component over a  $50^\circ$  range was not expected for a homogeneous polymer like PMPS- $\text{d}_3$ . For instance, with poly(vinyl acetate) the entire spectrum collapses into one broad line within about 10 degrees.<sup>9</sup>

Figure 2 shows the results of varying the echo delay at  $88^\circ\text{C}$ . The spectra retain their basic shape after about  $50 \mu\text{s}$ . The initial change from  $35\text{--}50 \mu\text{s}$  may be due to remnants of the mobile FID after the last  $90^\circ$  pulse. There is a moderate intensity drop at  $\pm 10 \text{ kHz}$  as the delay is increased. Similar spectra run at  $25^\circ\text{C}$  (not shown) do not have this intensity loss, suggesting that the loss is not from frequency dependent

$T_2$  relaxation.

## Discussion

At high temperatures, the spectra appear to be superpositions of a rigid and mobile component. Thus, the backbone motion could be modelled by a bimodal distribution of correlation times. Such a conclusion is supported by the x-ray and tacticity studies on PMPS- $\text{d}_3$  polymerized with  $\text{Na}^{1,2}$ . The x-ray diffraction pattern has three peaks suggesting three different domain sizes in the polymer and the tacticity studies indicate long runs of mm and rr triads. These domains and sequences may be related to the rigid and mobile fractions.

A broad distribution of correlation times might also account for the apparent two component behavior if it had significant intensity in both the fast and slow regimes. Without being bimodal, though, such a distribution would also have significant, if not more, intensity in the intermediate regime where the echo delay affects the spectrum. The spectra of Figure 2 do not appear to be greatly affected by the delay, but the intensity change as a function of frequency and delay for backbone motion superimposed on methyl rotation has not been calculated. Without this calculation or further experimental evidence, the possibility of a broad distribution covering both fast and slow regimes can not be eliminated.

## Conclusions

From the  $^2\text{H}$  NMR point of view (a kHz time scale), the  $T_g$  of PMPS- $\text{d}_3$  occurs over a broad range of temperatures. Preliminary investigations on the backbone motion in PMPS- $\text{d}_3$  may be in favor of a bimodal system. Undoubtedly, there is some sort of distribution of correlation times governing the system. However, the nature of the distribution has not been conclusively characterized by these two experiments. Further work on the types and rates of motion is underway.

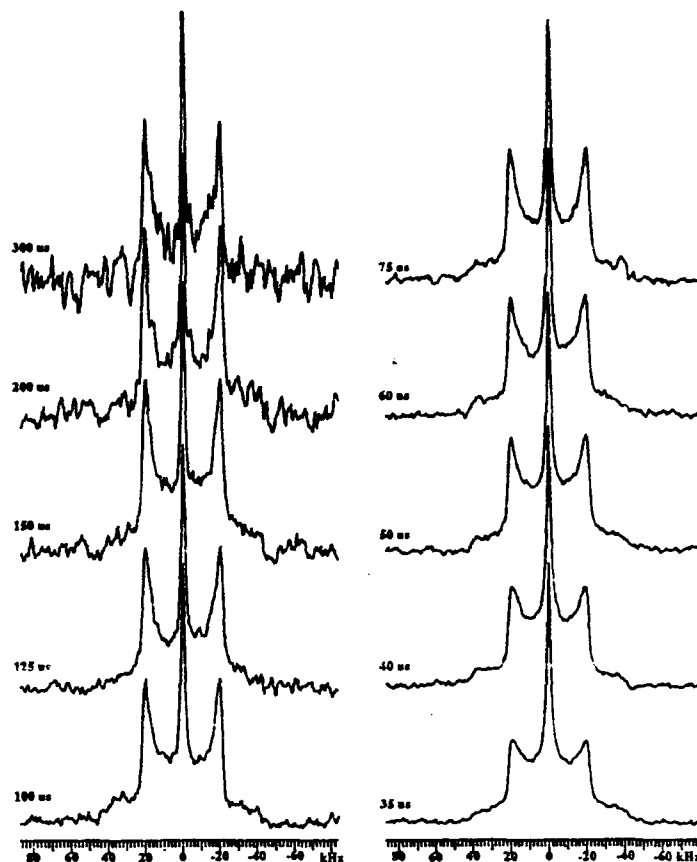


Figure 2. Solid echo spectra of PMPS- $\text{d}_3$  at  $88^\circ\text{C}$  with varying echo delays

## References

- 1) J. Maxka, F. K. Mitter, D. R. Powell, R. West, *Organometallics*, **10**, 660, 1991.
- 2) J. Maxka, R. West, R. D. Miller, personal communication.
- 3) H. W. Spiess, *Annu. Rev. Matter. Sci.*, **21**, 131, 1991.
- 4) A. Abragam, "The Principles of Nuclear Magnetism," Oxford Univ. Press, Oxford, 1961.
- 5) J. G. Powles, J. H. Strange, *Proc. Phys. Soc.*, **82**, 6, 1963.
- 6) H. W. Spiess, H. Sillescu, *J. Magn. Reson.*, **42**, 381, 1981.
- 7) H. Schmidbaur, *Chem. Ber.*, **124**, 1953, 1991.
- 8) Spectra similar to Figure 1 for poly(vinyl acetate)- $\text{d}_3$  have been taken in our labs.

## Acknowledgements

The authors acknowledge the financial support of IBM (FB, EG, RM) and the Office of Naval Research (RO,FB).